Structure and Dynamics of Octamethyl-ethinyl-ferrocene: a New Organometallic Rotator Phase
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Beamline: X3B1

Introduction: Substituted ferrocenes exhibit a variety of interesting properties, in view of possible applications (UV photocathodes, photochemical quenching agents, anionic photoinitiators), but also under more fundamental aspects of the properties of soft condensed matter. In particular, acetyl ferrocene was reported to exhibit a mesophase with translational symmetry but rotational disorder between the ordered crystalline and the liquid phase. Octamethyl-ethinyl-ferrocene (OMFA) exhibits a sharp decrease of the Lamb-Mößbauer factor well below the melting point. No single crystal X-ray diffraction data could be obtained at room temperature due to lack of suitable samples. The question about the microscopic nature of the phase transition can only be solved using high-resolution powder diffraction, since the extremely low number of Bragg reflections and the high diffuse background pointed to the existence of a rotator phase above the transition temperature.

Methods and Materials: High-resolution X-ray powder diffraction (at NSLS), quasielastic nuclear forward scattering (at Hasylab, ESRF), differential scanning calorimetry (in-house); Octamethyl-ethinyl-ferrocene

Results: All three methods yield a strong thermal hysteresis , the phase transition temperature is 248K on heating and ~220K on cooling.

X-ray diffraction data obtained at NSLS (Fig. 1) allowed us to determine the space group at room temperature (RT). Indexing with ITO led to a hexagonal unit cell (Z = 1) with the lattice parameters a = b = 12.9475(1) Å , c = 9.5578(1)Å, which in the rhombohedral setting correspond to a = 8.1258(1) Å , α = 105.63°. Since the rhombohedral angle is close to the tetrahedral angle of 109.47°, it was possible to deduce a related body-centered cubic packing with a "pseudo-cubic" unit cell parameter of 9.383 Å. The geometrical relations between the cubic and the rhombohedral unit cell and the locations of the OMFA molecules are depicted in Fig.2. The crystallographic density derived from these parameters is ρ = 1.161g cm^{-3}.
No extinctions were found in the powder pattern, indicating R3m as the most probable space group. This space group has a higher symmetry than would be compatible with a fixed arrangement of OMFA molecules, whose point symmetry is much lower in all possible conformations, which confirms the assumption of orientational disorder of OMFA in its RT phase.

Quasielastic nuclear forward scattering (QNFS), which is a novel and useful technique for the investigation of high wavevector modes in slow glassy relaxation in bulk, in nanoporous matrices and under pressure, as well as for the jump diffusion in intermetallics. It combines the extremely high energy resolution of Mößbauer spectroscopy with the favorable properties of a highly collimated synchrotron beam, and it provides information about slow dynamics on the ns-μs scale as well as about the fast dynamics (ps and faster) described
by the Lamb-Mößbauer factor. Using this technique at the beamlines PETRA1 (Hasylab) and ID18 (ESRF), we found out that below 246K the dynamics of the Fe atom associated with the phase transition is much slower than the QNFS timescale (~141 ns); at 246K, it enters the time window around 1μs; and at 248K, it immediately becomes so fast that it can not be monitored any longer by QNFS, but leads to a sharp decrease in the Lamb-Mößbauer factor.

Using differential scanning calorimetry, an order-disorder transition enthalpy of (9.85±1.05)J g^{-1} or (3186±340)J mol^{-1} was determined, corresponding to a transition entropy of (13.3±1.4)J mol^{-1} K^{-1} . In a very simple model, where all molecular orientations are energetically equal and have well-defined rotation angles for each minimum of the potential well, these values are compatible with but no proof for the assumption that the transition involves the onset of rotation of one of the cyclopentadienyl rings between five rotational conformations.

Conclusions: We conclude that the solid-solid phase transition in OMFA, as first determined by Mößbauer spectroscopy, is a first-order transition from a low-symmetry low-temperature phase to a high-symmetry high-temperature plastically crystalline phase with nearly cubic symmetry. Several questions remain:

1. Is the observed transition exclusively due to intramolecular degrees of freedom?
2.Does intermolecular steric hindrance come into play?
3.Are the involved degrees of freedom pure rotations of the cyclopentadienyl rings?

4.What is the structure of the low-temperature phase?
These questions have to be answered by further experiments.

References: T.Asthalter, H.Franz, U.van Bürck, K.Messel, E.Schreier, R.Dinnebier, accepted by J.Phys.Chem.Solids
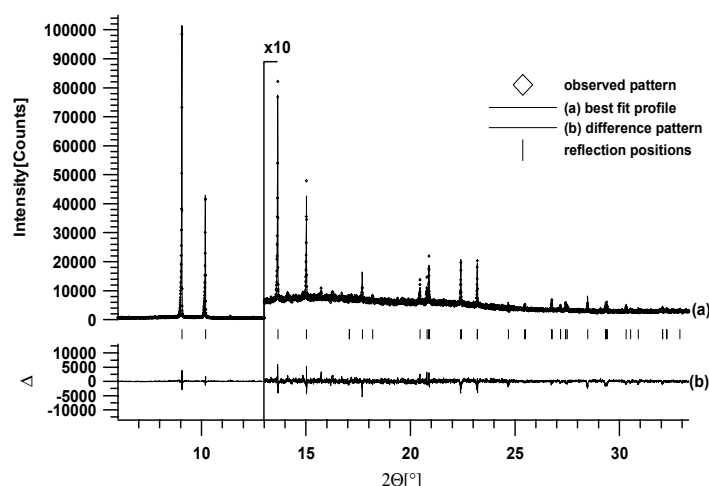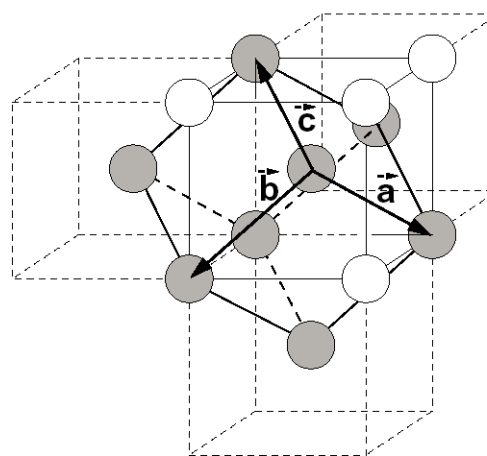

Fig. 1: XRD powder pattern for OMFA

Fig. 2: Rhombohedral vs. cubic unit cell